Oil Wastewater Coagulation with Industrial Waste Iron Coagulant

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Abstract

The study presents the results obtained during the coagulation of water with high content of oil compounds assessment as total petroleum hydrocarbon (TPH). Coagulation was carried out with a complex coagulation agent based on iron salts obtained from industrial waste. The control parameters of coagulation: turbidity, organic carbon (TOC), TPH, chemical oxygen demand (COD) in treated water samples with the optimal dose of coagulation agent based on iron salts obtained from industrial waste are similar to the residual values of the parameters determined in samples treated with the optimal dose of ferric chloride. The results obtained for the coagulation of oil wastewaters with optimal doses with different coagulation agents are supported also by the UV spectra. The advantage of the complex coagulation agent obtained from industrial waste was that it can be used for some wastewater in lower doses, by 25%, vs. ferric chloride.

Introduction

Oil compounds assessment as total petroleum hydrocarbon (TPH) ending up in the environment through contaminated water can cause many changes, degradation, and depreciation thereof. TPH wastewater contains organic load varying from a few hundred to thousands of $mgO_2 \cdot L^{-1}$, expressed by COD parameter. The pH of the wastewater is usually neutral[1-3]. One of the typical processes used as a primary treatment for this wastewater types is coagulation-flocculation process. Literature data on the quantities of pollutants removed by coagulation of wastewaters containing TPH are very different. In recent years the demand for recyclable material, environment friendly, increased in the treatment of waste water [1, 4, 5] . Studies done on total petroleum hydrocarbon wastewater resulting from the oil industry report the use of aluminum salts (alum, poly aluminum chloride.etc.), iron salts (ferric chloride or sulfate), etc., as coagulants [2, 6]. The studies consider the selection of optimal pH, and the coagulant dosage required to obtain the best possible performance in the process of coagulation. Coagulation pH was controlled and then adjusted with mineral base or acid. Coagulation studies are conducted in the pH domain 5.5 to 8.5. The optimal dose established was of tens $mg \cdot L^{-1}$of metal to several hundred metal $mg \cdot L^{-1}$. The efficiency of the removal of the color was in the range 86-91.3%, when using aluminum salts *i.e.* poly aluminum chloride, poly-aluminum zinc silicate chloride compared to the reduction efficiency due to the ferric chloride, which was 74-79%. The removal of the COD was performed with yields of 67-72%. The removal of suspensions was of 71.0-98.9% [2, 6]. In the present study were studied comparative total petroleum hydrocarbon wastewaters treatment with complex coagulation agent based on iron salts obtained from industrial waste vs. ferric chloride coagulant agent.

Experimental

Were studied wastewater input taken from the zone of the effluent wastewater from oil extraction scaffolding. Wastewaters containing TPH studied are apparent water color yellow-brown / brown and real shades of yellow. Wastewaters strong smell of petroleum products. They were in the range 33.5-72.5^{0}NTU turbidity. Wastewaters studied exhibit a pH in the range of 7.16-7.91.Wastewaters presents high loads of TPH. Total petroleum hydrocarbon are in the range 95.9-526.0 mg TPH$\cdot$L^{-1}. Organic load expressed by the TOC was in the range of 32.76-99.34 mg C$\cdot$L^{-1}. Organic load expressed by the COD does not express correctly the organic load. Wastewater COD values are in the range of 161.3-515.35.0 mg $O_2\cdot L^{-1}$. It is known that the oxidation of organic compounds with dichromate in strongly acidic medium (COD parameter) does not oxidize the aromatic substances probably heavily loaded in the studied wastewaters. Therefore by the low values of COD the organic load of these wastewaters cannot be properly assessed. The spectra drawn in the UV-VIS were performed on the filtered water. These waters show a range of absorption at 240-260 nm. A254 is specific absorbance at 254nm wavelength. Studied wastewater presents A254 range from 1.031 to 2.230 absorbance units (cm^{-1}). Coagulating agents used were: ferric chloride produced by Chimopar S. A. Bucharest and a complex coagulant based on iron salts obtained from industrial wastes in the absence/presence of aid coagulant: indigenous tuff originated from Zalau Quarry, Romania. Indigenous volcanic tuff contains 72% clinoptylolite. Coagulation was performed with a stirrer equipped with variable speeds (Phipps & Bird Company, USA). The optimal dose of the coagulation agents, in the absence / presence of coagulation aids for maximum pollutant removal, was done by Jar Test. The coagulation pH of the wastewater investigated was 7.0, corrected with hydrochloric acid or sodium hydroxide. In the supernatant separated from the treated water samples, conventional parameters were analyzed according to the standardized norms: pH determined by pH-meter model 290A ORION RESEARCH USA, turbidity with Micro 100 Laboratory Turbid meter, Scientific Inc. USA; COD by hot K dichromate oxidation in strongly acidic medium; TOC by TOC Analyzer with Multi N/C 2100 Analytic Jena, Germany. The absorbance – the unconventional parameter, at 254 nm wave length, A245, was analyzed by UV VIS spectrophotometer, Specord 205, Analytic Jena, Germany. Total petroleum hydrocarbons were determined according to the Romanian standardized norms by extraction with carbon tetrachloride (SR 7877-1) *i.e.* TPH is extracted from a volume, (V), of wastewater at pH=1 corrected with hydrochloric acid, d= 1.19 g$\cdot$L^{-1}, by mixing with solvent. Extracts number is four. Solvent extracts dried by passing through a filter with anhydrous Na_2SO_4 p.a. layer. Then solvent extracts are placed in capsule, with m_1 [g]. The solvent is evaporated and weigh the capsule with TPH residuum with m_2 [g]. Calculate the amount of TPH, TPH $g\cdot L^{-1} = (m_2 - m_1) \cdot V^{-1} \cdot 1000$. Studied waters must have the characteristics required by national norm GD 352/2005 - NTPA 002 to be discharged into the sewerage networks of localities *i.e.* solvent extraction compounds =30mg$\cdot$L^{-1}[7].

Results and Discussion

Table 1 shows an example of determining the optimal dose of ferric chloride for the a randomly selected wastewater with TPH content, by Jar Test method. As can be seen from Table 1 water samples treated with ferric chloride remain colored in yellow, probably because some of the components of the petroleum hydrocarbon in the water are not removed using ferric chloride as a coagulating agent. There is the likelihood that iron forms yellow chelates during coagulation thus giving the final color of the treated water. Optimal doses for ferric chloride for the studied wastewaters were between 12.0-24.0 mg Fe $\cdot$L^{-1}. Efficiencies of the coagulation process for the range of coagulation dosage 8.04-24.0 mg Fe $\cdot L^{-1}$, were 30.5 to 38.1% for the organic load expressed by parameter TOC, 67.1-73.4% for total petroleum hydrocarbon, and for turbidity of 64.1 to 76.1%. For COD, coagulation efficiencies were of 40.0 to 41.0%. Minimal dose to strongly reduce turbidity was at 12.06 mg Fe $\cdot L^{-1}$, see Table 1. For higher doses than 24.1 mg Fe $\cdot L^{-1}$, the colloidal system of the wastewater recovers.

Table 1. Optimal dose of ferric chloride coagulant for wastewater studied, at pH = 7.0; Wastewater characteristics: TPH = 95.9mg$\cdot L^{-1}$, TOC = 32.76 mg C $\cdot L^{-1}$, COD = 161.3mg$O_2 \cdot L^{-1}$, A254 = 1.031 cm^{-1}

No	Parameters	Treated samples					
		1	2	3	4	5	6
1	Dose[mg Fe $\cdot L^{-1}$]	4.0	8.04	**12.06**	16.08	24.1	28.0
2	Color	Yellow	Yellow	**Yellow**	Yellow	Yellow	-
3	Residual turbidity [NTU]	F	12.0	**8,.0**	8,2	8,2	23.0
4	Reduction efficiency [%]	51.6	64.1	**76.1**	75.5	75.5	31.8
5	COD[mg$O_2 \cdot L^{-1}$]	-	139.5	**95.34**	96.7	-	-
6	Reduction efficiency [%]		13.5	**41.0**	40.0	-	-
7	TPH [mg$\cdot L^{-1}$]	67.2	31.3	**29.9**	26.8	25.5	-
8	Reduction efficiency [%]	30.7	67.1	**68.1**	72.1	73.4	-
9	TOC [mg C $\cdot L^{-1}$]	29.7	21.33.	**22.6**	22.86	20.3	-
10	Reduction efficiency [%]	12.2	34.8	**31.1**	30.5	38.1	-

Table 2 presents the results obtained when determining the TPH wastewater optimal dose of complex coagulant based on iron salts obtained from industrial waste in the absence/presence of the coagulation aid: volcanic indigenous tuff.

Table 2. Optimal dose of complex coagulation agent based on iron salts obtained from industrial waste in the absence/presence of the coagulation aid: volcanic indigenous tuff. Coagulation pH = 7.0.

No.	Parameters	Treated samples				
		1	2	3	4	5
1	Dose [mg Fe $\cdot L^{-1}$]	3.0	6.0	**9.0**	15.0	**9.0 and aid tuff 0.5 g/l**
2	Color	Yellow	Yellow	**Colorless**	-	**Colorless**
3	Residual Turbidity [NTU]	16.2	15.2.0	**12.5**	11.0	**12.5**
4	Reduction efficiency [%]	51.6	54.6	**62.6**	67.1	**62.6**
5.	COD[mg$O_2 \cdot L^{-1}$]	-		**109.0**	109.0	**103.6**
6	Reduction efficiency [%]			**32.8**	**32.8**	**35.7**
7	TPH [mg$\cdot L^{-1}$]		41.3	**27.9**	26.8	**19.1**
8	Reduction efficiency [%]		56.9	**70.9**	72.0	**79.6**
9	TOC [mg C $\cdot L^{-1}$]	29.7	28.1	**18.6**	22.86	**12.9**
10	Reduction efficiency [%]	9.5	14.6	**43.2**	30.5	**60.4**

The optimal dose of complex coagulant based on iron salts obtained from industrial waste was 9.0 mg Fe $\cdot L^{-1}$. The advantage of the complex coagulant based on iron salts from industrial waste was that it required reduced optimal doses by 25% vs. the optimal doses of ferric chloride. Residual values of turbidity, TOC, TPH and COD in the water samples treated with the optimal dose complex coagulant based on iron salts obtained from industrial wastes are similar with the residual values of parameters determined in samples treated with the optimal dose of ferric chloride. Aid coagulant addition to the optimal dose of the coagulation with complex coagulant determined lower residual values for parameters TOC and TPH. Indigenous volcanic tuff addition to the optimal dose of coagulation with complex coagulant from industrial wastes caused an increase in the reduction efficiency of TPH from 70.9% to 79.6% and for TOC from 43.2% to 60.4%.These results are further confirmed by UV spectra shown in Figure 1. Figure 1 shows that treating the wastewater with the optimal dose of complex coagulation agent from industrial wastes in the absence of indigenous tuff determines 0.56 $cm^{-1}$for A254 and in the presence of tuff 0.46 cm^{-1}.

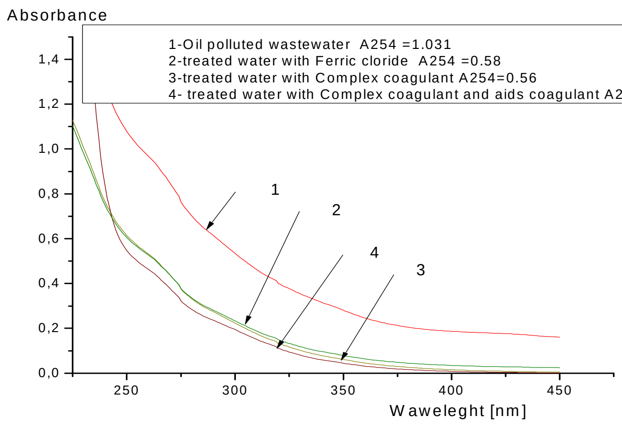

Figure 1. UV VIS spectra for untreated wastewater and treated samples with complex coagulation agent based on iron salts obtained from industrial wastes in coagulation aids absence/presence

Conclusions

The study compared the efficiencies of removing total petroleum hydrocarbon from wastewater obtained in the coagulation stage performed using a complex coagulation agent based on iron salts obtained from industrial wastes and a classic agent the ferric chloride showed that:1. The residual values of the turbidity, TOC, TPH and COD in water treated samples with the optimal dose of complex coagulation agent are similar to the residual values of the parameters determined in samples treated with the optimal dose of ferric chloride, 2.The addition of tuff to the optimal dose of complex coagulation agent caused lower residual values for the parameters TOC and TPH, 3.The efficiencies of the process of coagulation with various coagulating agents used are supported also by UV spectra, 4.The advantage of complex coagulation agent based on iron salts obtained from industrial wastes was that it required reduced optimal dose by 25%, vs. the optimal doses of ferric chloride.

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